Highly Crystalline Polyimide Particles

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ABSTRACT: Several kinds of highly crystalline polyimide particles were obtained by heating polyamic acid solutions at 180°C that induced the thermal imidization of polyamic acids in *N*-methyl-2-pyrrolidone (NMP). The morphology of the particles was a sheaf or coral type that was similar to a polymer spherulite. The WAXD analysis revealed that the particles were highly crystalline. The size of the particles was in the range from 1 μm to 10 μm . It was concluded from the electron diffraction studies that the molecular axis of polyimide in the (PMDA/PPD) particle lay perpendicular to the sheaf surface.

KEY WORDS Highly Crystalline Polyimide / Polyimide Particle / Spherulite / Polyamic Acid / Thermal Imidization /

Aromatic polyimides exhibit remarkable thermal and mechanical stabilities as one of the commercialized engineering plastics. The rigid type of polyimides are generally difficult to mold because the rigid polymer chains are not soluble in any solvents and the crystalline phase cannot be molten by heating. Recently, many types of polyimide films have been prepared by the casting or the imidizing method of polyamic acid for the purpose of high performance applications in the electronic or aerospace fields.^{1–3}

The rigid chain polymers such as poly(*p*-phenylene-benzobisthiazole) or poly(*p*-oxybenzoyl) were isothermally crystallized from their dilute solutions.^{4,5} Also, the spherulite of poly(*p*-phenyleneterephthalamide) was prepared from the concentrated sulfuric acid solution.⁶ Furthermore, a new type of thermoplastic polyimide was synthesized and the spherulite of this polymer was prepared by the isothermal crystallization technique from the melting polymer near to T_m .^{7–9}

Also, spherulitic highly crystalline polyimide particles were obtained by the thermal imidization of polyamic acid in good solvent.¹⁰ Especially, the polyimide particles of rigid poly[(4,4'-oxydiphenylene)pyromellitimide] showed a unique sheaf- or coral-like morphology prepared by the thermal imidization of the precursor polymer in a good solvent.

In this report, several polyimide particles of rigid polymer chains were prepared by the thermal imidization of their precursor polymers in a good solvent, and the properties of the particles were characterized on the basis of FT-IR, X-ray and electron microscopic studies, and finally the formation mechanisms of the fine particles were discussed.

EXPERIMENTAL

Monomers and Reagents

Pyromellitic dianhydride (PMDA) was purchased from Mitsubishi Gas Chemical, and 3,3',4,4'-biphenyl tetracarboxylic anhydride (BPDA) was used as received from Mitsubishi Kasei Co., Ltd. Diamines of *p*-phenylenediamine (PPD) and 4,4'-diaminodiphenylether (DPE)

were also purchased from Mitsui Toatsu Co., Ltd. The chemical structures of the monomers are shown in Table I. The purity of all monomers was over 99%.

Preparation of Polyamic Acid

Polyamic acids as the precursors of polyimide particles were obtained by the polyaddition reaction of diamines and anhydrides in an aprotic solvent at 20°C under a N_2 atmosphere. The chemical reaction is shown in Scheme 1. For example, PMDA as Pyromellitic dianhydride was gradually added with stirring into the solution

Table I. Chemical structures of monomers for polyimides

Monomers	
Dianhydrides (Abbreviation)	Diamines (Abbreviation)
(PMDA)	(PPD)
(BPDA)	(DPE)

Scheme 1. Synthesis of polyimides via polyamic acids as precursors.

N-methyl-2-pyrrolidone (NMP) of PPD at 20°C under a N₂ atmosphere. The molar ratio of PMDA/PPD was adjusted to be one in order to get a high molecular weight polyamic acid. The inherent viscosity of polyamic acid was around 2.0 dl g⁻¹ after the reaction of 2 hours.

Preparation of Polyimide Particles

Polyimide particles were gradually precipitated by heating a polyamic acid/NMP solution at 180°C for 2 hours because the synthesized polyimides was insoluble in solvent (NMP). The particles were repeatedly washed with acetone and water and then, dried at 100°C after filtration. The stepwise heat treatment was carried out up to 400°C in a dryer for 1 h to complete the imidization reaction.

The yields as the particles were almost 70% for the (PMDA/PPD) system and 90% for the (BPDA/PPD) one. For reference, a polyimide film was prepared by imidization of the solvent cast film from the polyamic acid solution. The heat treatment of the polyimide films was also carried out by stepwise heating up to 400°C. During the heat treatment, the polyimide film was clamped at all edges of the film with the iron frame. The thickness of the film was about 50 μm.

Characterization of Particles

The morphology of the polyimide particles was observed using a scanning electron microscopy (SEM; HITACHI S-400) and a transmission electron microscope (TEM; HITACHI H-500), which were used to analyze the structure of the particle. The electron diffraction (ED) pattern was also taken by TEM. IR spectra were recorded using a FT-IR spectrophotometer (Nicolet 20SXB). The sample was sealed in a KBr pellet, and also the polyimide thin films on the KRS cell were used for IR measurement as a reference. Elemental analyses of the particles were carried out using a CHN analyzer (YANAGIMOTO MT-3).

The aggregation structure of the polymer chains in the particle or the film was investigated by wide angle X-ray diffractometry (WAXD; RIGAKU RINT 1000). The casting films of the particles coagulated by a 10% collodion solution were used. The 10 pieces of polyimide films were piled up to be 0.5 mm thick as a reference.

The density of the molded pellet of the particles made by 1 ton cm⁻² pressure was determined in bromoform/ethanol solution at 30°C using a pycnometer. The thermal properties of the particles were evaluated on the basis of thermogravimetry and differential scanning calorimetry (RIGAKU TG-DSC).

RESULTS AND DISCUSSION

Properties of Highly Crystalline Polyimide Particles

Polyimide particles were precipitated and obtained by the thermal imidization of polyamic acids in good solvents. The morphology of the particles was slightly different depending on the kind of polyimides with different chemical shown in Table II.

Figure 1 shows the SEM photographs of the prepared polyimide particles for the PMDA/PPD, BPDA/PPD, and PMDA/DPE polyimides. The shape of the particle was like a sheaf of about 1 μm long for the (PMDA/

Table II. Structures of polyimides

Abbreviation	Structure of polyimide
PMDA/PPD	
BPDA/PPD	
PMDA/DPE	

PPD). The (BPDA/PPD) and the (PMDA/DPE) particles look like a coral structure of 5 μm in diameter. The morphology of Figures 1(b) and (c) indicate a radial crystal growth from the center of the particles. Such a morphology of the polyimide particles were similar to that of the spherulite of an usual polymer.^{11,12} The differences in the particle morphology might be attributed to those in the packing states of polyimide molecules during the crystallization growth. The chain packing states is strongly related to the rigidity of polymer chain in a solution. The diameter of these particles could be controlled by the heating temperature of the polyamic acid solution or by changing the concentration of the polymer solution during the heating process.

The FT-IR spectra of the particles showed the absorption bands of the imide group at 730 cm⁻¹, 1710 cm⁻¹, and 1780 cm⁻¹, of which bands observed at the corresponding wave numbers also in the case of the conventional polyimide films.

The density, the diameter and the elemental analyses data of the particles are summarized in Table III. The contents of carbon, hydrogen and nitrogen in the particle are almost comparable with those of the calculated compositions based on the chemical structure of polyimide. The density of each particle was higher than that of the corresponding polyimide film. This indicates that the crystallinity of the particle is higher than that of the film.

In 1960s, the polyimide powders or particles for molding applications were already prepared by the chemical imidization of polyamic acid by dehydration reaction through the acetic acid anhydride/pyridine as dehydration reagents.¹³ The prepared powder through such a process was like a mechanically milled particle and the large particles over 50 μm diameter were obtained. The morphology of the particle was not spherulitic as shown in Figure 2.

Structure of Crystalline Polyimide Particle

Figure 3 shows the WAXD profiles of three kinds of polyimide particles, and also the corresponding polyimide films. The sharp diffraction peaks from the crystal plane were observed in the case of the particles. This clearly indicates that the crystallinity of the particle was

Figure 1. SEM photographs of polyimide particles prepared from (a) PMDA/PPD, (b) BPDA/PPD, and (c) PMDA/DPE.

Table III. Properties of polyimide particles treated at 400°C

polyimides		Density g cm ⁻³	Diameter ^a [mean] μm	Elemental analyses			
				C %	H %	N %	O %
PMDA/PPD	Particle	1.65	1	64.1	2.5	9.7	23.7
	Film	1.55	—	(66.2)	2.1	9.7	22.1) ^b
BPDA/PPD	Particle	1.63	5	68.3	2.3	7.4	21.5
	Film	1.47	—	(69.1)	2.6	7.3	20.9) ^b
PMDA/DPE	Particle	1.59	5	72.2	3.1	7.7	17.0
	Film	1.42	—	(72.1)	2.7	7.7	17.5) ^b

^a From SEM observation. ^b Calculated from chemical structure of polyimides.

higher than that of the corresponding polyimide film. Also, the difference in the WAXD patterns between particles and film might be strongly related to the difference in the polymer chain orientation in the spherulite and the film as well as the degree of crystallinity. The orientation of the polymer chain in the film tends to be in the in-plane direction because of the molecular

Figure 2. SEM photograph of PMDA/DPE powder prepared by chemical imidization with acetic anhydride/pyridine.

alignments parallel to the film surface by the shrinkage of film under the clamping of the film's edge during the imidization, so it is assumed that the polyimide molecule lies parallel to the film surface. Then, WAXD patterns

Figure 3. X-Ray diffraction diagrams of polyimide particles and films.

Table IV. Unit cell parameters of polyimide particles

Abbreviation (polyimide)	Unit cell parameters (nm)		
	<i>a</i> -axis	<i>b</i> -axis	<i>c</i> -axis
PMDA/PPD	0.834	0.541	1.24
BPDA/PPD	0.826	0.628	1.52
PMDA/DPE	0.658	0.475	3.12

of through view (TV) and edge view (EV) for the polyimide films would be fairly different with those of random view for the particles as shown in Figure 3.

The unit cell parameters of the polyimide particles are summarized in Table IV from the analysis of the WAXD and ED results. These almost corresponded to those of the already reported values for the unidirectional polyimide film published in previous reports.^{14,15} TEM photographs and ED patterns are shown in Figure 4 for the PMDA/PPD, BPDA/PPD, and the PMDA/DPE leaf. The incident electron beam was normal to the leaf surface, and the sharp diffraction spots from the (110) and (200) planes were observed in the ED photograph for the (PMDA/PPD) which indicated that the polyimide molecules were regularly stacked perpendicular to the leaf surface in the spherulite.

The thickness of a leaf was almost 10 nm based on the SEM observations, which implied that the polymer chain might be folded or terminated near the leaf surface. The arrangement of the molecular chain for the (PMDA/

PPD)particle is shown as the model structure in Figure 5. Also, the sharp diffraction patterns of the crystal plane were observed in the ED photographs for the (BPDA/PPD) and the (PMDA/DPE) spherulites as shown in Figure 5. In this figure, it seemed that there were many diffraction patterns from a few crystal systems, and the polymer chains were also stacked perpendicular to the leaf surface in the particle.

The molecular chains of these polyimides are rigid, however, the polymer chain may be folded at the leaf surface which was observed in the usual polymer spherulites such as polyethylene or polystyrene. If the folding of a polymer chain was taken out in a leaf, it could be considered that the amic acid group in the polymer chain might be present near the leaf surface making it easier for folding of the polymer chain.

Thermal Properties of Particles

Figure 6 shows the TG curves of the polyimide particles. The weight change were slight up to 400°C. The weight losses started at about 500°C, resulting in the formation of pyrolyzed polymer. Then, the final particles became to be highly heat resistant. The TG curves were slightly different among three kinds of particles; the (PMDA/DPE) particle showed the lowest heat resistance among them. The chemical structure of the (PMDA/DPE) polyimide is slightly flexible because of containing the ether bonding in the structure as compared with the other types of polyimides, so the heat resistance of this particle may show lower than those of

Figure 4. TEM and ED photographs of (a) PMDA/PPD, (b) BPDA/PPD, and (c) PMDA/DPE particles.

Figure 5. Model structure of PMDA/PPD particle.

others.

Recently, there have been many reports on carbonized polyimide films for the purpose of the formation of a graphite film.¹⁶⁻¹⁸ In general case, crystalline polyimide particles are carbonized by thermal degradation. Actually, our polyimide particles were changed to the carbon particles with a yield of 50% by heating them up to 1000°C. The morphology of the obtained carbon particles was very similar to that of the polyimide particles as precursors in spite of the extremely abrupt decomposing process. As discussed above, the polyimide chains were stacked perpendicular to the leaf surface in the particle, and the thermal decomposition chains might be occurred in the intramolecular part of the polyimide chain as described in the case of the carbonization of the

Figure 6. Thermal gravimetric curves of polyimide particles prepared from (a) PMDA/PPD, (b) BPDA/PPD, and (c) PMDA/DPE.

polyimide film. Therefore, it is reasonable to consider that each leaf in the spherulites would be thinned by the thermal degradation, and the shapes of the leaf, in other words, the particle did not change during the carbonization process.

CONCLUSIONS

New highly crystalline polyimide particles were obtained by a precipitation process when heating a polyamic acid solution. These were prepared as a result of the thermal imidization of polyamic acid in a good solvent.

The morphology of the particles was such that a sheaf or coral was similar to the spherulite of the polymer, and these were recognized to be highly crystalline particles from the analysis of their physical properties.

The electron diffraction pattern indicated that the molecular chains of the polyimide lay perpendicular to the leaf surface in the spherulite as the polyimide particle.

These particles had a unique spherulitic morphology,

remarkable thermal properties of the polyimide, and turned to carbon particles by the thermal decomposition of polymer chains.

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